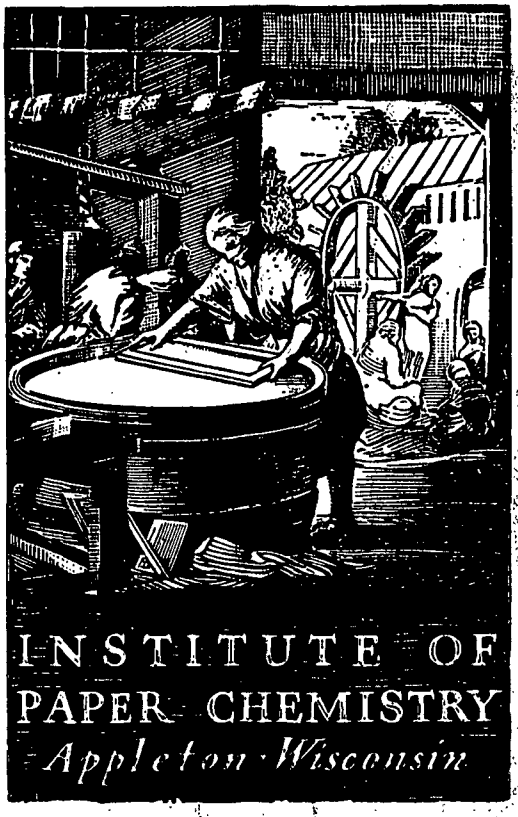

A FUNDAMENTAL STUDY OF POLYMER FLOCCULATION AND RETENTION AIDS

Project 3143

Report Four

A Progress Report

to

MEMBERS OF GROUP PROJECT 3143

January 20, 1975

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

A FUNDAMENTAL STUDY OF POLYMER FLOCCULATION AND RETENTION AIDS

SUMMARY

This report covers investigations of the flocculation of TiO_2 and of the retention of TiO_2 on fibers in paper formed in a handsheet mold and on the IPC web former.

The amount of polyphosphate dispersant adsorbed on the TiO_2 particles was found to be only a fraction of the total amount present and to decrease with dilution. This behavior helps to explain some of the changes in zeta potential seen in the previous report during handsheet formation. A special apparatus was designed to permit separation of flocculated from unflocculated TiO_2. The zeta potentials of the separated materials were found to differ from each other at all degrees of flocculation. This was attributed to imperfect mixing of the suspension with the flocculant.

Handsheets containing TiO_2 were prepared with a number of cationic polyelectrolytes as retention aids. With one exception it was possible to correlate the amount of polymer necessary to achieve maximum retention with the charge density on the polymer as mirrored by its zeta potential. Experiments utilizing classified and unclassified pulp showed that most of the TiO_2 is initially retained by the pulp fines. For good filler retention enough cationic polymer must be present to provide good retention of the fines, also. A general trend of decreasing particle specific scattering coefficient with increasing particle retention was explained in terms of the higher probability of filler particle aggregation under conditions of greater surface concentration of the

TiO_2. Filler retained on a second, more highly beaten pulp produced a particle specific scattering coefficient about 20% less than that for the less highly refined pulp studied previously. The decrease was attributed to reduction in filler optical efficiency due to coating with excess fines. This explanation was verified by scanning electron micrographs.

The IPC web former was operated at 0.2% pulp consistency with polymer retention aids of two different molecular weights being added. The point of polymer addition and the vacuum applied to the suction box were the other major variables. Both percentage ash and particle scattering coefficient exhibit a dependence on polymer concentration with an optimum at about 0.15% based on the pulp. As found also in the handsheet studies, the molecular weight of the polymer has little, if any, effect on retention. As expected, the percentage ash and sheet specific scattering coefficient decrease with increasing suction box vacuum (increasing drainage rate) but no effect of retention aid molecular weight on the resistance to loss of particles via hydrodynamic shearing was seen. Good formation was found for all paper made, but addition of the polymer to the stock chest rather than in-line after the fan pump provided the better formation. Drainage increased monotonically with increasing polymer concentration over the range covered. It was, thus, not possible to maximize retention and drainage simultaneously with the particular polymer employed.

A summary of the important findings detailed in earlier reports of this project concludes this report.

INTRODUCTION

This is the final progress report for the present project. It covers the work of the last quarter and includes a summary of the more important conclusions reached in the earlier progress reports.

The objective of the project was to develop an understanding of the molecular and operational parameters pertinent to the use of polymers as retention aids in papermaking and as flocculation aids in the treatment of paper mill effluents. The research proceeded along several parallel tracks.

Flocculation studies were carried out on TiO_2 using a number of polymer systems. In the present report further investigations are described concerning the use of the zeta potential as an indicator of the state of flocculation of the TiO_2 system.

The major parameters examined in the retention studies were the molecular weight of the retention aid and the intensity of agitation during sheet formation. Two different methods of sheet formation were used for these studies. A correlation of polymer charge density (as revealed by zeta potential measurements) with retention was obtained from standard handsheet formation experiments. The IPC web former was used to study the interrelation between the molecular weight of the retention aid and the resistance to loss of retention caused by the hydrodynamic shearing forces of drainage. This machine permits realistic consistencies of several tenths of a percent to be used.

FURTHER STUDIES ON THE ZETA POTENTIAL OF PARTIALLY FLOCCULATED TiO_2

THE EFFECT OF DILUTION ON THE TiO_2 DISPERSANT

In the previous report (1) a strong change in zeta potential with dilution was found even in the absence of fines (cf. results for rayon in Table VII of that report). This suggested that the amount of dispersant on the TiO_2 particles was a function of the concentration of the filler. The type of TiO_2 used in this work (RG-grade, The Glidden Company) is vended as a dry powder with a polyphosphate dispersant already added. Previous work (2) had shown that addition of still more polyphosphate would result in decreased dispersion as noted by an increased viscosity at a constant percentage solids suspension.

A series of experiments was performed to determine the fraction of the polyphosphate that was bound to the surface of the TiO_2 particles as a function of particle concentration. The standard test for orthophosphate (PO_4^{-3}) was used (3) with the polyphosphate being first converted to orthophosphate by reaction with concentrated sulfuric acid and ammonium persulfate. In this analysis an antimony-phosphate-molybdate complex is formed whose concentration was obtained by measuring the absorbance at 880 nm on a Beckman DK-2 Ratio Recording Spectrophotometer. A calibration curve was prepared from the data on standard phosphate solutions.

Suspensions of various concentrations were made by dilution from a 7.4 wt.% stock suspension. These were centrifuged to remove the TiO_2 particles (and the polyphosphate bound to them), and the supernatant was analyzed for phosphate. A sample of a TiO_2 suspension was also treated with the reagents without removing the TiO_2 to determine the total polyphosphate present. Upon conversion of the dispersant to orthophosphate and complexation of the latter,

the TiO_2 flocculated and was removed by centrifuging. The absorbance of the supernatant was then read. The total polyphosphate as $P_3O_{10}^{-5}$ was 0.074% based on the TiO_2.

The fraction of the polyphosphate bound to the TiO_2 as a function of suspension concentration is shown in Fig. 1. As the suspension is diluted the amount of dispersant on the surface of the TiO_2 continuously decreases. During handsheet formation the furnish is sequentially diluted from 1-1/2% to 1/2% to 0.04% consistency. At an addition level of 5% on the pulp, the corresponding TiO_2 concentrations are 750, 250, and 20 mg/l, respectively. Hence, during the dilutions according to Fig. 1 the amount of polyphosphate on the surface decreases by more than half. This would likely affect the zeta potential. Whether the dispersant being lost from the surface would concomitantly lower the amount of cationic polymer adsorption, or whether the released polyphosphate would be bound to the adsorbed polymer at a greater distance from the TiO_2 surface it is not possible to determine. The result in either case would be a less positive zeta potential. As discussed in the previous report (1) other factors contributing to the decrease in zeta potential are adsorption of sulfate ion and of submicroscopic fines by the positively charged polymer. Indeed, experiments with only pulp and polymer (no TiO_2) exhibit similar decreases in the zeta potential of the fines upon dilution, suggesting that one of the latter mechanisms is operative here. For a furnish with all the components present, the electric double layer around a particle must be the result of a complex admixture of the aforementioned effects.

From the total amount of polyphosphate present, the amount of polyethylenimine (PEI) necessary to just neutralize the negative charge can be calculated. This should correspond to the point of zero zeta potential when

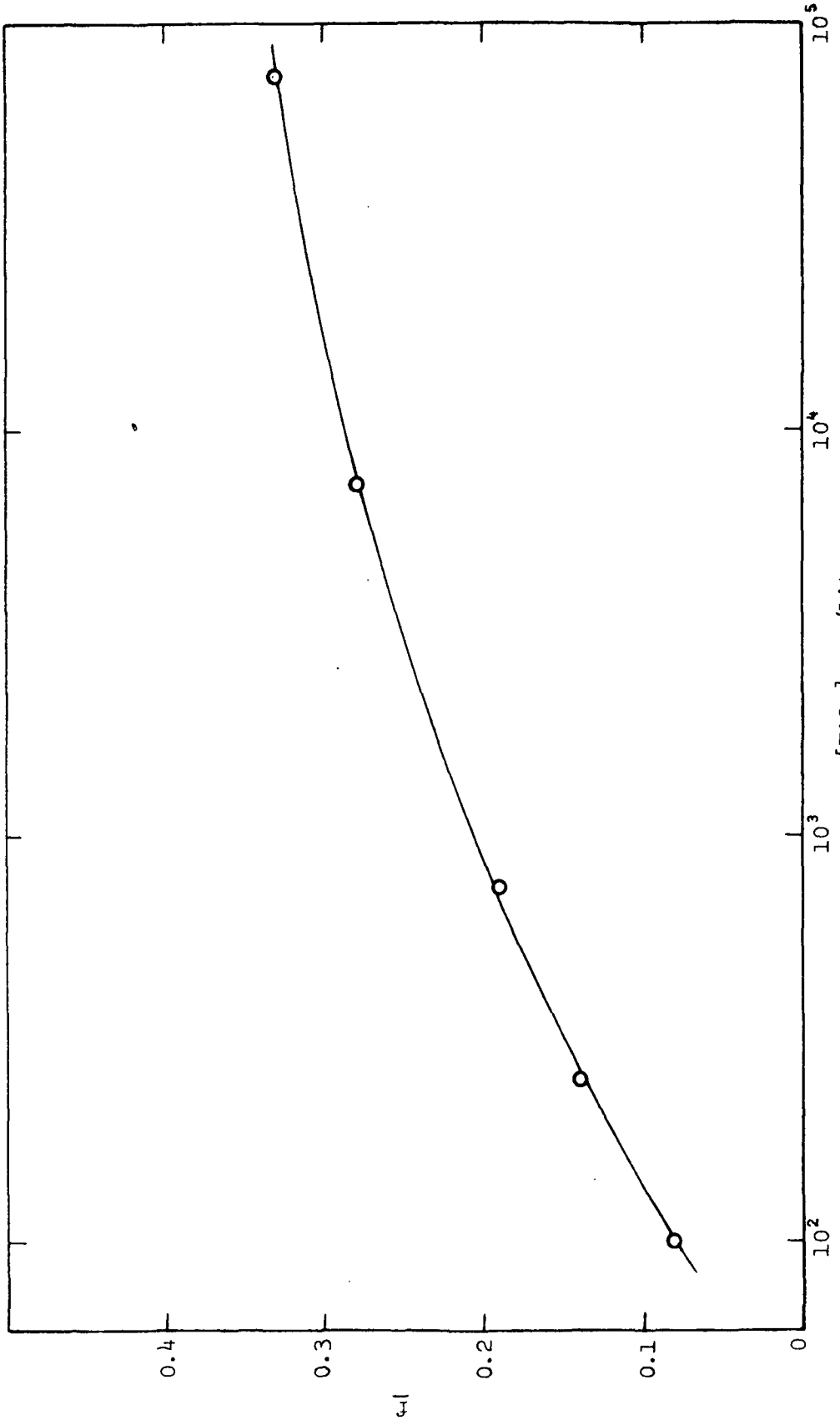


Figure 1. Fraction of Polyphosphate Bound to the Filler Plotted Against Concentration of TiO_2 (Logarithmic)

TiO_2 is mixed with PEI. Two assumptions are necessary: a) that the dispersant is present in the form $P_3O_{10}^{-5}$ and b) that the PEI interacts with the polyphosphate in solution as well as that on the TiO_2 surface. For the case of 1000 mg/liter TiO_2 at pH 5 the total number of negative charges per liter due to the polyphosphate is 8.8×10^{18}. The amount of PEI necessary to produce a like number of positive charges at pH 5 is 1.14 mg/liter. This value is in good agreement with the experimental result given in Fig. 8 of Project Report Two (4) where about 0.9 mg/liter PEI are required to reach the point of zero zeta potential. Since the isoelectric point of TiO_2 with no dispersant has been shown (5) to be at pH 6.4, it would be expected that the TiO_2 would contribute a small positive charge at pH 5. This could possibly account for the slight difference between the two values presented above. Again assuming that the PEI interacts equally with the polyphosphate in solution and that bound to the TiO_2 surface, the above results require that in the region of good flocculation the TiO_2 particles must bear a net negative charge. This is in agreement with the data shown in Fig. 8 cited above and gives further weight to the concept of the patch model of flocculation (1,6,7). It might still be argued that, due to possible inefficient initial mixing of polymer and suspension and the irreversibility of polymer adsorption, different particles within the system may carry different net charges. Some further experiments bearing on this question will be discussed in the next section.

ARE THE ZETA POTENTIALS OF FLOCCULATED AND UNFLOCCULATED TiO_2 THE SAME?

In the previous work (1) the zeta potentials of the sediment and supernatant portions of a partially flocculated TiO_2 dispersion were compared. The sediment was found to be consistently less negative than was the supernatant.

The former was obtained by centrifuging followed by redispersion of the sediment in distilled water at the same pH. In light of the results of the previous section it can be recognized that this procedure is erroneous, since it amounts to a dilution with a consequent change in the fraction of polyphosphate on the surface. A modified procedure was devised as follows. A system was prepared with the same composition of TiO_2, polymer, and pH as that under consideration. It was then centrifuged at high speed until a particle-free supernatant hereafter identified as "clear supernatant" was produced. This solution containing the same concentration of all ions as the original suspension was then used for preparing dispersions of sediment. Experiments showed a definite difference between the zeta potentials of a sediment slurried up in distilled water at the same pH and in clear supernatant. The former was more negative as might be expected from the results on the dilution of the paper furnishes cited previously (1).

A second problem concerned the method of obtaining the sediment. As mentioned above, this procedure consisted of a centrifugation step followed by a redispersion of the compacted sediment in clear supernatant. This latter step proved troublesome and an alternative method obviating the compaction was sought. A large stopcock with a 15-mm bore was fixed in a vertical position and closed at the lower end of its adjoining tube with a rubber stopper as shown schematically in Fig. 2. With the stopcock open, section C and the stopcock bore B were filled with clear supernatant (about 38 ml total). Upon thermal equilibration the stopcock was closed and a freshly prepared, partially flocculated TiO_2 suspension was introduced into section A (about 30 ml). After thermal equilibration to minimize convection currents, the stopcock was slowly opened, and the flocculated TiO_2 particles settled under gravity through B into C. When a

sufficient quantity had entered C the stopcock was again closed. As the rubber stopper was subsequently removed, the inrushing air caused thorough mixing of the sediment which was caught in a beaker and transferred to the Zeta Meter cell. The contents of section A were given a gentle centrifuging to remove flocculated particles, and were diluted with clear supernatant, if necessary, before having their electrophoretic mobility measured. This method allows a facile separation of flocculated and unflocculated material in a form ready for zeta potential analysis.

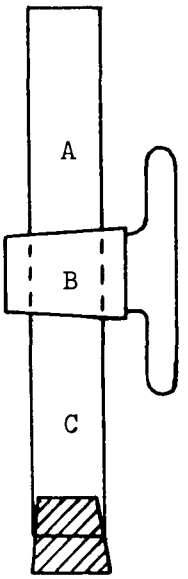


Figure 2. Schematic of Flocculation Fractionator

A series of TiO_2 suspensions (1000 mg/liter) partially flocculated with varying amounts of PEI at pH 5 was prepared by vigorous mixing for 5 minutes. The particles were fractionated with the apparatus described above and the zeta potentials were measured. The results are given in Table I along with the transmittance T of the supernatant obtained as described previously (4).

From the trend of the transmittance with concentration of the flocculant, it is apparent that the series begins near complete flocculation and extends into the region of restabilization. As noted before there is a consistent

difference between the values of the zeta potential for the flocculated and unflocculated species, the former in all cases being less negative. As emphasized previously, the optimum flocculation occurs between strongly negative particles. Because the untreated TiO_2 particles all have the same zeta potential, the only obvious explanation for the differences in Table I lies in an uneven distribution of the PEI molecules among the TiO_2 particles. In view of the virtually irreversible adsorption of the polymer, this must take place in the initial mixing step.

TABLE I

ZETA POTENTIALS OF PARTIALLY FLOCCULATED TiO_2

[PEI], mg/l	ζ (Supernatant), mv	ζ (Sediment), mv	$\underline{T}$, μa
0.53	-33	-24	151
0.6	-32	-23	118
0.7	-28	-16	12
0.8	-34	-12	3
1.0	+15	+18	3

In an attempt to verify the inefficient mixing hypothesis, a similar experiment was carried out using alum as the flocculant. Here, because of their small size and relatively low charge (compared with PEI), the complexed aluminum ions would be expected to adsorb reversibly on the TiO_2 and, no matter how poor the initial mixing, to produce particles with common zeta potentials. A system composed of 1000 mg/liter TiO_2 and 5 mg/liter alum produced a transmittance of 154 μa indicating good flocculation. The zeta potentials for the sediment and supernatant were -15 and -7 mv, respectively. The difference between these is outside experimental error and is, moreover, in the opposite direction to the results in Table I. It must be concluded that the interactions in the

TiO_2/flocculant system are not well understood at present, and that the zeta potential can only be used as a gross indicator of the state of the system until a better understanding is reached.

It should be mentioned that some changes of zeta potential with time have been noted and all measurements reported above have been taken at an approximately constant elapsed time to minimize these effects. The changes may by due to a gradual reequilibration of polyphosphate between surface and water under the influence of the added flocculant. Ideally, the zeta potential should be measured during the flocculation process, but this does not seem feasible at present.

HANDSHEET STUDIES OF RETENTION

MATERIALS AND METHODS

In addition to the polymers used as retention aids in past work (1,4), two more polyelectrolytes were examined. One was a cationically modified polyacrylamide, having a molecular weight of about 3 million and with about 4-6% of the monomer groups bearing a tertiary amine group. This polymer, to be denoted as PA-1 was included as a material with low charge density whose effects might be compared with those (1) of PA-2 and PA-3, cationically modified polyacrylamides having a high charge density. The other material was a cationically modified guar gum, having a relatively low charge density. This polymer with a polysaccharide structure might be expected to behave somewhat differently than the other retention aids which have (except for chitosan) essentially hydrocarbon backbones and polar side groups. The various polymers are identified in Appendix I.

For both of these polymers, immediate strong flocculation occurred when the retention aid was added at a level of 20 mg/40 g pulp to the TiO_2 suspension. It will be recalled (1,4) that this method of addition (i.e., polymer to TiO_2, rather than polymer to pulp plus TiO_2) resulted in slightly better retention and opacity for most of the polymers examined and was the usual method of addition. Apparently, the low charge density of PA-1 and the modified guar prevents the restabilization of the TiO_2 particles with a positive charge, and, therefore, these polymers were added to the pulp prior to the addition of the TiO_2.

For the comparison of the various retention aids, the beaten bleached softwood kraft (Pulp I) with a Canadian freeness (8) of 400 cc was used. The freeness of this pulp after dewatering and storage for a number of months was

445 cc in deionized water. For the web former runs to be discussed in a later section, a large quantity of homogeneous beaten pulp was required. Since insufficient quantities of Pulp I were available, a second pulp was obtained. This was a 50/50% blend of bleached kraft softwood and hardwood pulps beaten to a freeness of 40°SR in tap water (9). After dewatering and storage for several months at 5°C this material (Pulp II) had Canadian freenesses of 260 cc in tap water and 185 cc in deionized water. Hence, Pulp II, in addition to the different composition, was somewhat more refined than Pulp I.

Experiments to measure the relative charge density of the two pulps were performed by mixing the pulps at 1/2% consistency with various amounts of PEI-2 for five minutes with a Lightnin' stirrer. The white water passing through a 100-mesh screen from the furnish was centrifuged as necessary to obtain a slightly turbid suspension whose electrophoretic mobility was then measured with the Zeta Meter.

Since relatively large quantities of TiO_2 were required for the web former runs, a more rapid method which eliminated the fractionation step was devised. The required amount of TiO_2 was slowly added to enough water in a Waring Blendor at slow speed to give a 70% solids suspension. This was then treated for two minutes at high speed in the blendor and the resulting slurry was diluted to about 8% solids. This method produced a uniform TiO_2 suspension which will be denoted TiO_2(II). The earlier material which was dispersed by a less violent manner of mixing and which included a fractionation step (8) will be henceforth identified as TiO_2(I). Handsheet studies revealed little, if any, difference between these two filler preparations.

Previous work (1) and that described in an earlier section of this report showed that the zeta potential changed with dilution but that retention appeared to be governed by the conditions prevailing at the time the pulp, TiO_2, and polymer were first mixed together. This suggested that it might be more useful to measure the zeta potential at this point (1-1/2% consistency). A sample of the furnish after the five-minute mixing period and just before the dilution to 1/2% was poured through a 100-mesh screen, and the zeta potential of the resulting filtrate was determined and denoted ζ_f. The zeta potential of the white water from sheetmaking was also measured for comparison with previous results and will be identified as ζ_w.

To gain a quantitative measure of the distribution of the TiO_2 on the pulp, the specific scattering coefficient for the filler s_2 was calculated. The total scattering for the sheet s can be written as

$$s = w_1 s_1 + w_2 s_2 \qquad (1)$$

where s_1 is the specific scattering coefficient of the pulp (obtained by forming sheets with no TiO_2 present) and w_1 and w_2 are the weight fractions of pulp and filler in the sheet, respectively. Equation (1) can be rearranged and s_2 can be expressed in terms of the measured quantities s, R, and s_1. The last-named is just the value of s for handsheet set No. 1 (4).

$$s_2 = (2000/R)(s - s_1) + s_1 \qquad (2)$$

The factor 2000 accounts for the fact that the TiO_2 dose was 5% on the pulp and that the retention R is expressed in terms of percent.

RESULTS AND DISCUSSION

The results not reported previously for handsheets formed from Pulp I and TiO_2(I) are listed in Table II, while those for Pulp II and TiO_2(II) are given in Table III. Values for the percentage retention, specific scattering coefficients of the sheet and of the pigment, and the zeta potentials of the furnish (1-1/2%) and of the white water are presented as functions of the polymer additives.

Effect of Charge Density of the Polymer on Retention

The values for the (white water) zeta potential as a function of polymer concentration for a number of cationic polymers exhibited a parallel behavior (vide Fig. 7 of Progress Report Three). This suggested that by suitable shifts along the horizontal axis (by a constant amount for a given polymer) all of the data might be reduced to a single curve. Because the abscissa is a logarithmic scale this shift corresponds to multiplying each concentration by a factor γ which is a constant for a given polymer. Since the greatest range of concentrations was measured for the PEI-2, this polymer was arbitrarily chosen as the reference material and, hence, its γ is by definition equal to unity. The data for the other cationic polymers, including those for PA-1 and modified guar, were shifted to superpose on the PEI-2 curve and the shift factors γ determined. The reduced curve is shown in Fig. 3 where the shift factors, in the order of increasing magnitude, for the individual polymers are also listed. The superposition, with the exception of a couple of errant points, is good. The parameter γ may be viewed as proportional to an effective charge density of the polyelectrolyte or better as an indicator of the ability of the polymer to modify the zeta potential of the TiO_2 and pulp surfaces. In this role the geometry of the polymer chain (linear or branched) and possibly the "stiffness" of the polymer backbone, as influenced by chemical structure and intramolecular repulsion of

TABLE II

HANDSHEET PROPERTIES

[Pulp I, TiO_2(I)]

Set No.	Additive Type	Additive Amount, mg/40 g pulp	ζ_f, mv	ζ_w, mv	R, %	s, cm^2/g	s_2, cm^2/g
62	Chitosan[a]	26		-21	68	543	6020
69	PEI-1[b]	50		-20	60	531	6440
84	PEI-2[c]	60		-21	85	575	5690
85	PEI-2[d]	60		-9	80	577	6060
88	PEI-1[b,e]	6.7		-22	64	506	5250
89	PEI-1[b,f]	6.7		-28	32	452	6710
90	PEI-2[f]	70		-19	80	561	5680
96	PEI-1[g]	50		-20	66	542	6190
97	Chitosan[h]	26		-25	60	522	6150
144	PA-3[i]	50	0	-21	84	421	2070
145	PA-3[j]	50	+14	-17	86	417	1930
149	PEI-2[k,a]	50	+13	-22	79	586	6330
153	Guar[k,l]	20	-20	-30	33	448	6420
154	Guar[k,l]	20	-25	-26	39	476	6930
155	Guar[k,l]	40	-24	-31	50	503	6460
156	Guar[k,l]	60	-39	-23	55	528	6860
157	Guar[k,l]	80	-27	-25	60	537	6570
158	Guar[k,l]	100	-25	-27	60	527	6280
174	PA-1[k,l]	20	-26	-27	43	480	6390
175	PA-1[k,l]	40	-32	-26	51	502	6300
176	PA-1[k,l]	60	-40	-22	60	520	6100
177	PA-1[k,l]	80	-22	-24	66	533	5950
178	PA-1[k,l]	100	-24	-32	70	542	5830
179	PA-1[k,l]	120	-30	-29	68	540	5970

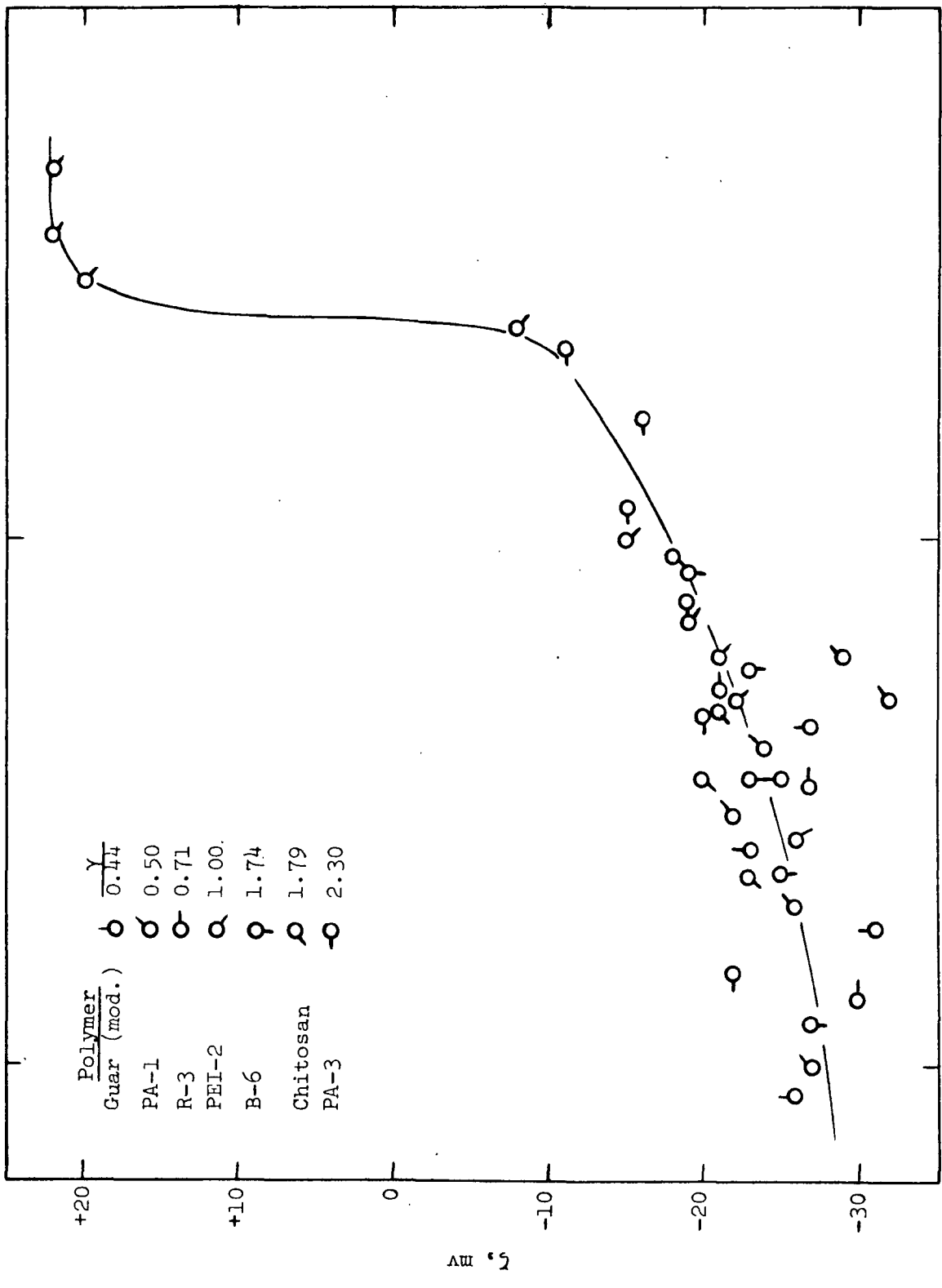
[a] Polymer added to furnish after TiO_2.
[b] pH of TiO_2/PEI adjusted from 9 to 5 before adding to pulp.
[c] 50 mg Polymer added to TiO_2, 10 mg polymer added to furnish 1 min before dilution to 1/2%.
[d] 50 mg Polymer added to TiO_2, proportion of 10 mg polymer added to deckle box.
[e] Classified pulp.
[f] 50 mg Polymer added to TiO_2, 20 mg polymer added to furnish 1 min before dilution to 1/2%.
[g] 6.7 mg Polymer added to TiO_2, 43.3 mg polymer added to pulp before addition of TiO_2/polymer.
[h] 6.5 mg Polymer added to TiO_2, 19.5 mg polymer added to pulp before addition of TiO_2/polymer.
[i] TiO_2 and polymer mixed at pH 7.
[j] TiO_2 and polymer mixed at pH 5.
[k] TiO_2(II).
[l] Polymer added to pulp followed by TiO_2.

TABLE III

HANDSHEET PROPERTIES

[Pulp II, TiO_2(II)]

Set No.	Additive		ζ_f, mv	ζ_w, mv	R, %	s, cm^2/g	s_2, cm^2/g
	Type	Amount, mg/40 g pulp					
146	No TiO_2, no polymer		-19	-26	--	338	--
147	No polymer		-22	-24	15	389	7180
148	PA-3	40	-9	-19	74	506	4850
150	PA-3	20	-15	-34	56	475	5230
151	PA-3	60	0	-17	77	516	4970
152	PA-3	80	+17	-18	75	510	4950
159	PA-2	20	-14	-31	63	488	5070
160	PA-2	40	0	-21	70	514	5350
161	PA-3	100	+20	-15	82	524	4900
162	PA-2	60	+4	-13	75	522	5270
163	PA-2	80	+9	-19	78	525	5130
164	PA-2	100	+18	-14	78	529	5240
165	PA-4	20	-14	-20	58	478	5170
166	PA-4	40	-10	-18	68	489	4770
167	PA-4	60	+12	-20	75	520	5220
168	PA-4	80	+24	-10	80	518	4840
169	PA-4	100	+23	-14	80	522	4950
170	PEI-2	20	-12	-22	67	481	4630
171	PEI-2	40	-11	-15	80	531	5180
172	PEI-2	60	+10	-12	88	533	4750
173	PEI-2	80	+16	-16	84	531	4910


ζ, mv
+20
+10
0
-10
-20
-30
10
100
Yc, mg/40 g pulp
Polymer
Guar (mod.)
Y
0.44
PA-1
0.50
R-3
0.71
PEI-2
1.00
B-6
1.74
Chitosan
1.79
PA-3
2.30

charged groups, will likely be important factors in addition to that of charge density. The geometry and stiffness of the macromolecule determine the volume over which it will exert the electrostatic forces resulting from a given amount of charge on the polymer.

If γ is a measure of the effectiveness of a given polymer for retention, it would be expected that all the polymers would achieve maximum retention at the same value of reduced concentration γc. The data of Fig. 6 of Progress Report Three (1) have been replotted in Fig. 4 as percentage retention against reduced concentration. The data for PA-1 and modified guar have been included, also. To reduce confusion most of the individual data points have been omitted. Except for the polymer PA-3 the maxima in retention fall within a narrow range of γc. To emphasize this point, the actual concentration $(c)_m$ and reduced concentration $(\gamma c)_m$ at the point of maximum retention are presented in Table IV.

TABLE IV

CONCENTRATION OF POLYMER AT MAXIMUM RETENTION

Polymer	c_m, mg/40 g pulp	γc_m, mg/40 g pulp
Modified guar	92	41
PA-1	108	54
R-3	85	60
PEI-2	50	50
B-6	31	54
Chitosan	26	46
PA-3	70	160

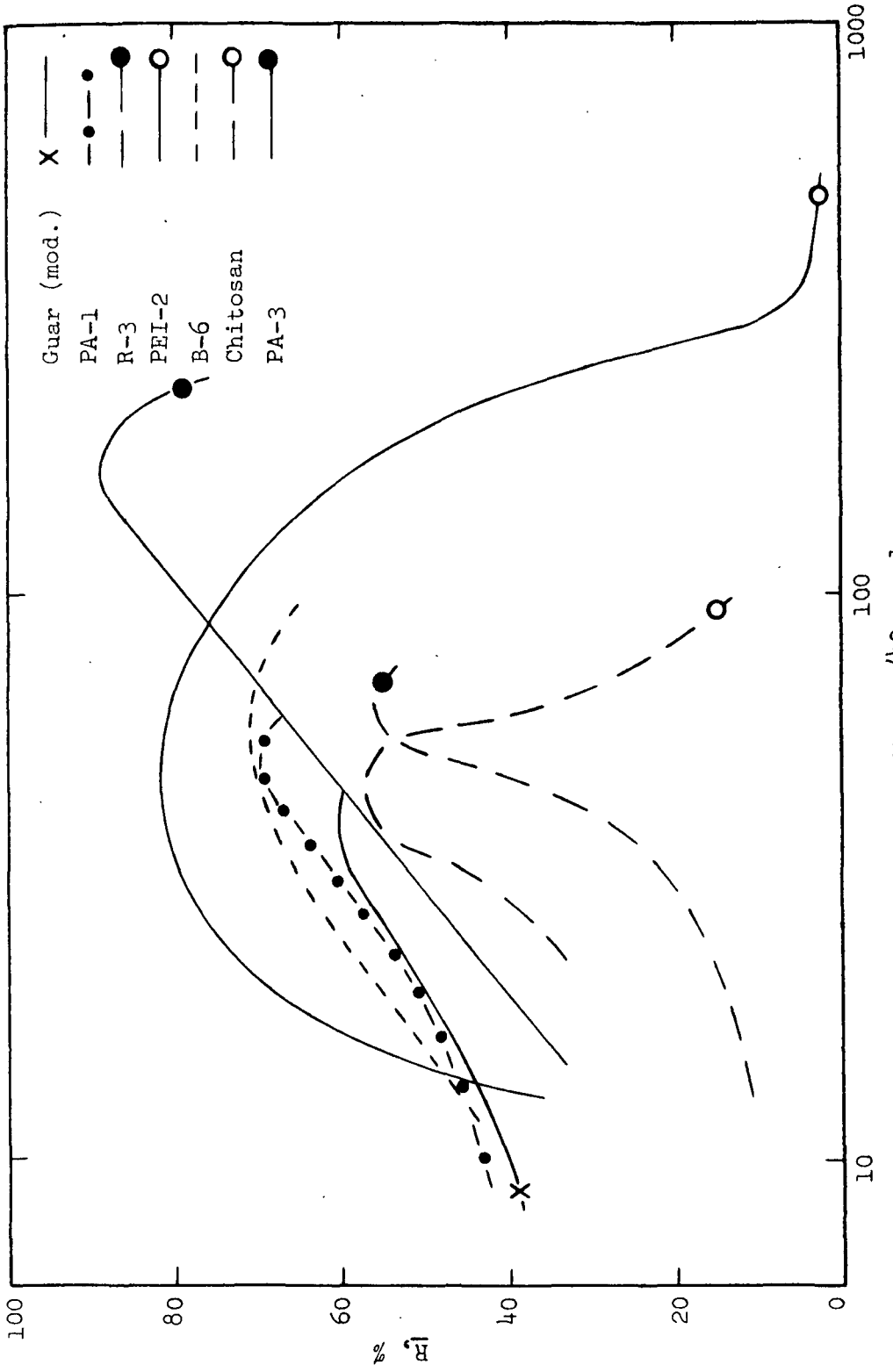


Figure 4. Retention Plotted Against Logarithm of Reduced Concentration for the Indicated Polymers

It is apparent that the same shift factors which superpose the zeta potential data (with the exception of that for the PA-3 polymer) determine the concentration range of maximum potential for enhancing retention. The reason for the discrepancy of the one material is not evident at present. It is also apparent that neither the zeta potential data nor any other presently available can predict the maximum level of retention achievable with a given polymer. As seen in Fig. 4 these can range from about 60 to almost 90%. Further work must be undertaken to ascertain the relationships between polymer structure and effectiveness toward retention.

Effect of Fines on the Retention Process

It might be thought that to achieve good retention it is only necessary to combine a positively charged filler with a pulp having a negative zeta potential. Set 89 illustrates this case where TiO_2 has been coated to saturation with highly charged PEI molecules and then mixed with the pulp. The retention was only 32%. The same conditions of polymer and TiO_2 were also used (Set 88) with a classified pulp described elsewhere (1). Here the retention was 64% showing the strong influence of the fines. From these results the following sequence of events can be inferred. When a positively charged filler is mixed with a negatively charged pulp, the TiO_2 coflocculates with both the fibers and the fines. The interactions with the latter are likely the larger of the two because (1) the fraction of the total surface area attributable to the fines is large compared with their weight fraction, and (2) the velocity of the fines is much larger than that of the fibers (due to the larger mass of the latter) and, hence, the number of collisions with pigment particles is greater. This means that the fines retain most of the TiO_2. Hence, the furnish conditions must be made favorable to the retention of the fines by the fibers. This is achieved by

adding excess cationic polyelectrolyte (beyond that needed to render the TiO_2 positive) in order to decrease the negative charge or zeta potential of the fines and fibers. Compare the result (Set 5) of adding 7.5 times as much PEI as was used with Set 89. At this concentration, the optimum for this polymer and (unclassified) pulp, the retention was 71%. To reiterate, merely having positively charged filler particles is not enough. Sufficient polymer must be added to provide for coflocculation of the fibers and fines. Thus, the best conditions for the retention of filler and of fines go hand in hand.

Effect of Furnish Conditions on the Particle Scattering Coefficient s_2

In this section the effect of several variables on the optical efficiency of the TiO_2 will be examined. In the last report, a difference between the sheet specific scattering coefficient s of two furnishes (one where the polymer was added to the TiO_2 and the other where the polymer was added to the furnish — pulp plus TiO_2) was attributed to a difference in pH in the two systems at the time of polymer addition. Since two variables were involved in that study, point of polymer addition and pH, the experiment was repeated with pH being the sole parameter. The polymer was added to the TiO_2 after both had been previously adjusted to the same desired pH. After it was mixed for 5 min, the TiO_2/polymer was added to the pulp as usual, and the pH was adjusted to a final value of 5. The results are presented numerically in Table V and graphically in Fig. 5.

The progressive increase in aggregate size with decrease in pH is readily apparent. The corresponding decrease in particle scattering coefficient is as expected. The explanation given previously (1) was that addition of polymer at high pH (low charge on the polymer) gave a protective colloid effect until the pH was subsequently lowered after the TiO_2/polymer was added to the

furnish. Mixing of the polymer and filler at lower pH (higher charge on the polymer) gave a system which readily flocculated before addition to the pulp. By adding the polymer to the furnish at pH 7 (Set 139) the TiO_2 flocculation was not so severe because of the competition of pulp for the positively charged TiO_2/polymer. The point remains that the furnish conditions at the moment of polymer addition determine the scattering efficiency of the filler. Their effect on the polymer charge and on the interaction between polymer and filler must be known in order to maximize opacity.

TABLE V

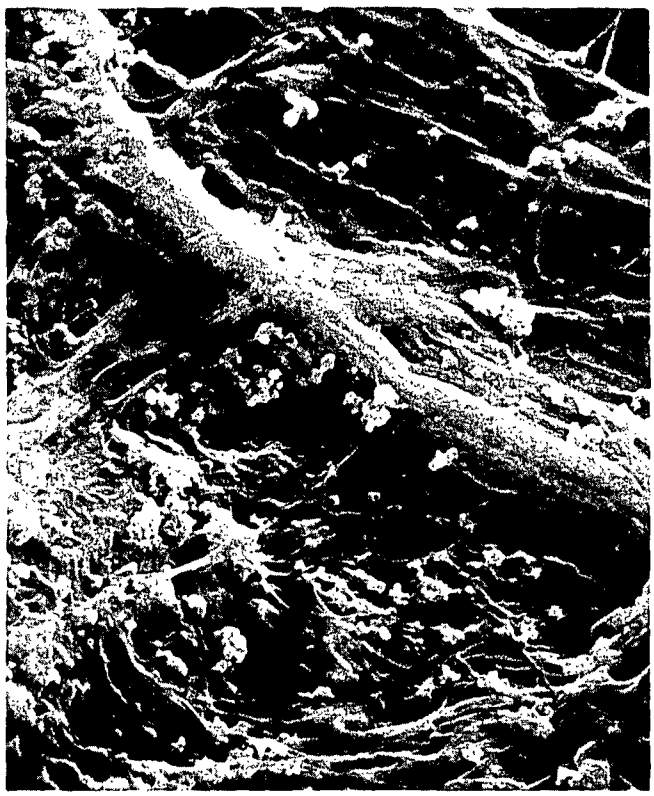
EFFECT OF pH ON HANDSHEET PROPERTIES

(50 mg PA-3/40 g pulp)

Set	pH	$\underline{R}$, %	$\underline{s}_2$, cm^2/g
138	10	83	5800
139[a]	7	80	5050
144	7	84	2070
145	5	86	1930

[a]Polymer added to pulp plus TiO_2.

It is of interest to examine the broad range of furnishes studied during this project for trends which may be difficult to ascertain over a more limited range of variables. A salient feature was that the samples with poor retention tended to possess the highest particle scattering coefficients suggesting a functional relationship between these two parameters. For ease of reference, the data are repeated in Table VI with sets of a given polymer grouped together. Sets at the same concentration represent either duplicates or different order of addition of components, point of addition, etc., which information



a

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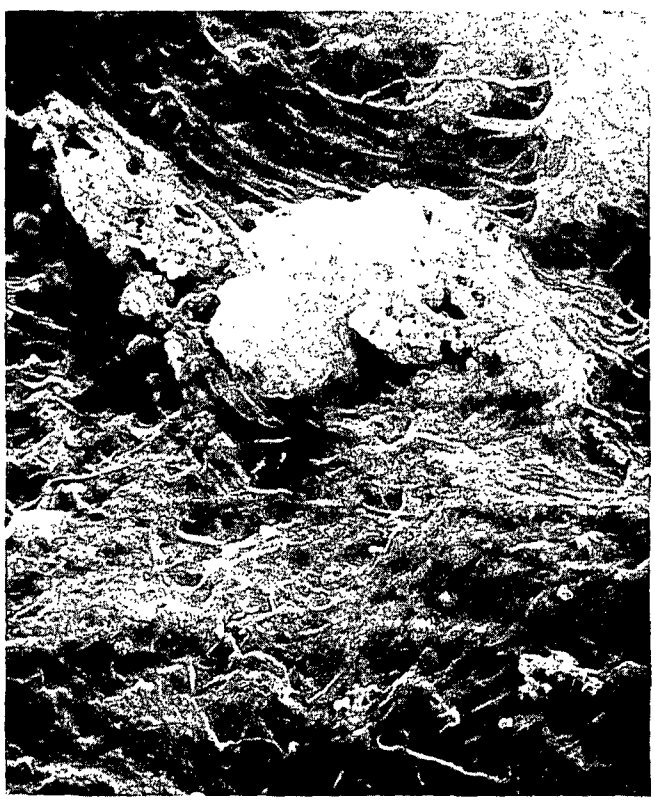


c

d

Figure 5. SEM Micrographs of Handsheets from Sets a) 138, b) 139, c) 144, and d) 145. Magnification 6000X

may be found in the original tables [Table II of this report, Table IV (1), and Table II (4)]. Values for the particle scattering coefficient for the samples in Table VI without an X have been plotted against percentage retention in Fig. 6. A clear trend of decreasing $\underline{s}_2$ with increasing retention is apparent. It is entirely reasonable that, as the density of TiO_2 particles on the surface of the fibers increases (that is, increasing retention), the probability that additional TiO_2/polymer/fines will adsorb in juxtaposition to that already present increases. The increase in effective particle size leads to a decrease in optical efficiency. Further evidence for this is given by the results (triangles in Fig. 6) for the handsheets with 10% (rather than 5%) TiO_2 based on the pulp added to the furnish. Here the percentage ash or number of particles per unit surface area of fiber is much higher and the corresponding values of $\underline{s}_2$ are depressed. The straight line in Fig. 6 is not meant to imply a linear relationship between the variables but is only added to point up the trend. Although most of the data fall fairly close to the "average line," there are notable exceptions. For example, Sets 91 and 135 provide >60% retention while maintaining high values of scattering. Figure 7 shows a scanning electron micrograph of the surface of Set 91. The distribution of particles over the fiber surfaces is very good, and the particles are present for the most part as individuals or small clumps. Note, however, the large aggregate in the upper right-hand corner. This figure may be compared with the sheets in Fig. 5 having much lower particle scattering coefficients. An understanding of the reason for the much better than average optical efficiency for these deviant samples would be most important but must await further work.

Mention must now be made of the data identified by an X in Table VI which were not included in Fig. 6. These fall into two categories. The first

TABLE VI

SELECTED HANDSHEET PROPERTIES

Polymer	Set No.	Amount, mg/40 g pulp	R, %	s_2, cm^2/g
PEI-1				
	37	6.7	25	7360
	89	6.7	32	6710
	36	13	49	7070
	35	27	62	6610
	3	50	73	6130
	4	50	68	6010
	5	50	71	5920
	39	50	16	8250
	69	50	60	6440
	70	50	77	6440
	96	50	66	6190
	7	100	65	5910
	9	200	57	6080
X	10	400	46	6030
X	11	500	28	6690
X	12	600	29	6630
X	13	750	25	6220
PEI-2				
	38	13	37	7320
	75	27	77	6400
	42	50	82	5910
	149	50	79	6330
	84	60	85	5690
	85	60	80	6060
	90	70	80	5680
	66	100	74	5930
X	18	250	32	5680
X	22	250	32	5720
X	21	310	9	5680
X	20	375	4	5480
X	17	500	3	4050
R-3				
	47	72	23	7020
	59	72	37	6250
	60	72	70	5790
	55	97	74	5440
Chitosan				
X	49	13	54	5390
	91	19.5	72	6870
	61	26	77	6430
	62	26	68	6020
	97	26	60	6150
	71	39	49	6250
	83	52	35	6570
PA-4				
X	119	6.7	53	1600
	115	33	81	5360
	110	50	85	5520
	132	73	82	6040
	129	100	70	5760

Polymer	Set No.	Amount, mg/40 g pulp	R, %	s_2,
PA-3				
X	120	6.7	34	4
	140	20	64	5
	116	33	72	5
	111	50	82	5
	138	50	83	5
	133	73	89	5
	130	100	79	5
PA-2				
X	121	6.7	34	5
	117	33	81	5
	112	50	82	5
	134	73	88	5
	131	100	68	6
B-6				
	122	6.7	44	6
	136	13.3	59	6
	135	20	62	7
	118	33	71	6
	113	50	67	6
Modified guar				
	153	20	33	6
	154	20	39	6
	155	40	50	6
	156	60	55	6
	157	80	60	6
	158	100	60	6
PA-1				
	174	20	43	6
	175	40	51	6
	176	60	60	6
	177	80	66	5
	178	100	70	5
	179	120	68	5
PEI-2 (10% TiO_2)				
	126	27	63	5
	123	50	82	5
	124	100	79	4

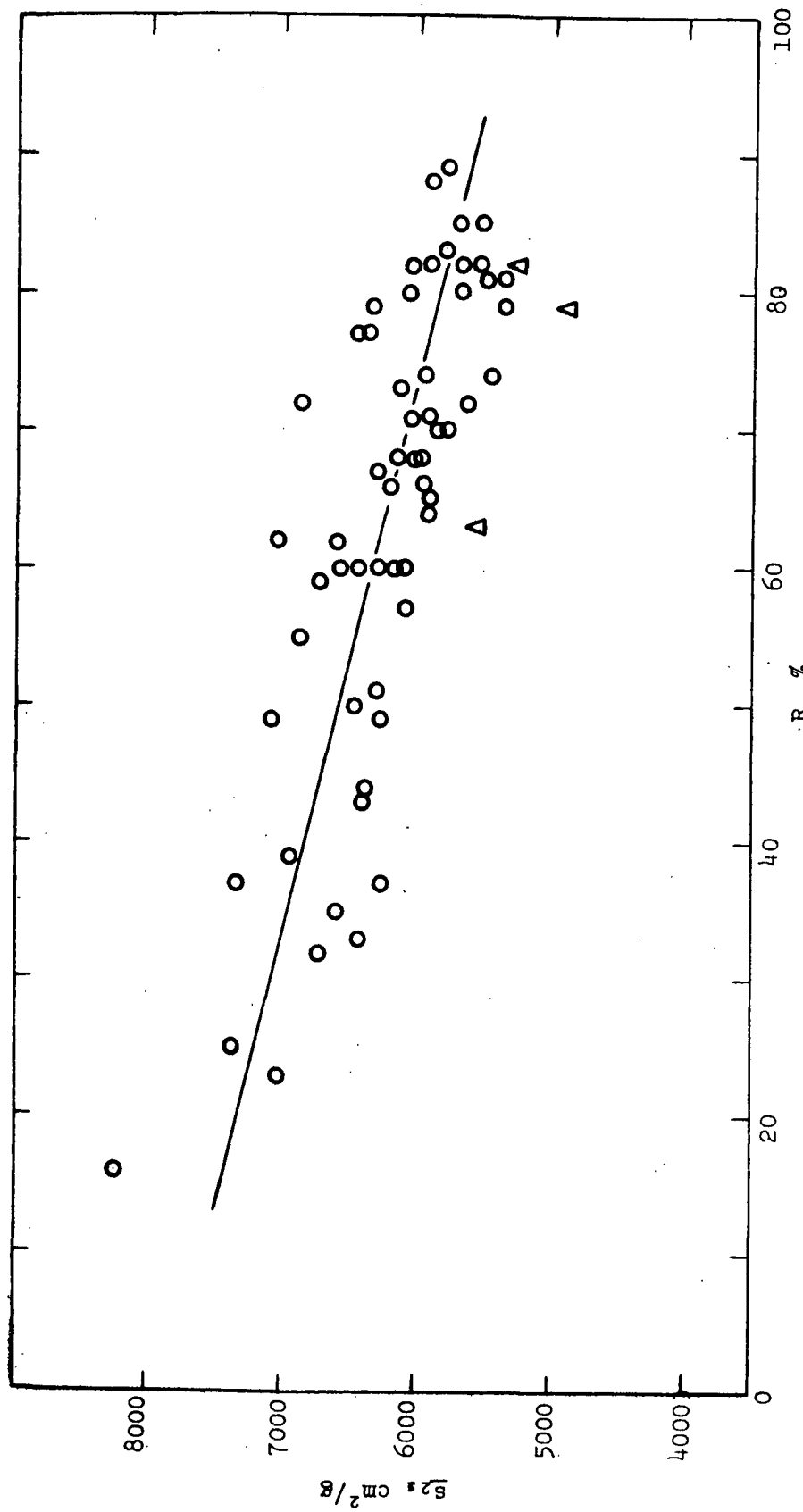


Figure 6. Particle Scattering Coefficient Plotted Against Percent Retention. Triangles Indicate Sets with 10% TiO_2 in Furnish

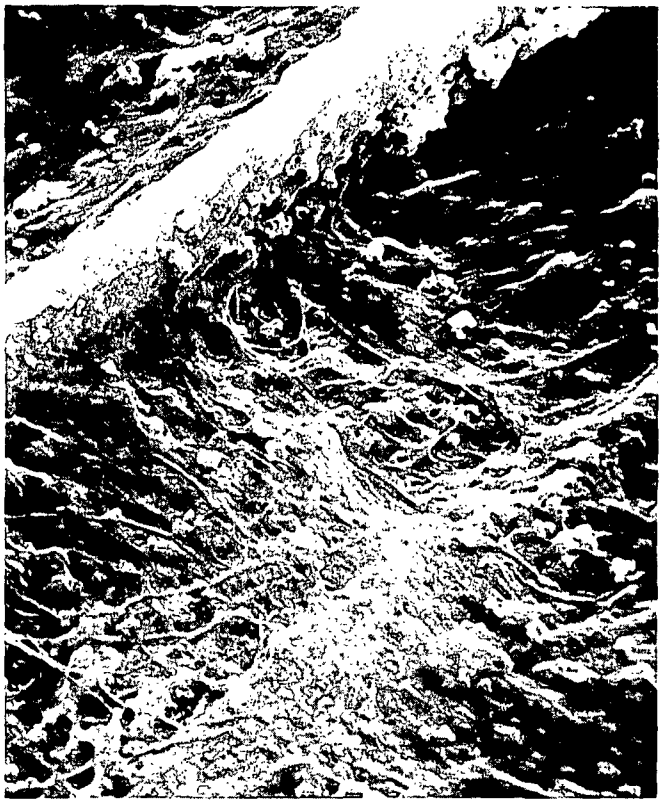


Figure 7. SEM Micrograph of Handsheet from Set 91. Magnification 6000X

includes the lowest concentration for chitosan and for PA-2, PA-3, and PA-4. These data fall considerably below the average line drawn. It is most likely that some preflocculation of the TiO_2 occurred when the polymer was initially mixed with the pigment. The polymer solution was added at a rapid but finite rate to the TiO_2 suspension, and during the earliest portions of addition the TiO_2-to-polymer ratio passes through the flocculation region. At higher polymer concentrations the time the system spends in the flocculation region is correspondingly shorter, and the data fall about the average line. In hindsight, it would have been preferable to have added the TiO_2 slurry to the polymer solution instead of vice versa to maintain a high polymer to TiO_2 ratio at all times and thereby prevent flocculation.

The other samples which appear to fall consistently below the average are those at the very high concentrations of PEI-1 and of PEI-2, well past the optimum for retention. In this region the zeta potential is close to zero or positive, but the explanation for the decreased scattering efficiency is not evident.

Comparison of Two Pulps

In addition to characterizing the pulps, the data below afford a comparison of the effect of the pulp on the properties of the handsheet.

The charge density or the "cationic polymer demand" of the two pulps was measured by determining the zeta potential of the pulps (fines) at 1/2% consistency treated with various amounts of PEI-2. No TiO_2 was present during these measurements. The results are shown in Fig. 8 with the two pulps behaving quite differently. As might be expected, the more highly beaten pulp requires more cationic polyelectrolyte to attain zero zeta potential. The explanation for the radically different shapes of these "pulp titration" curves is not evident from the limited amount of data available.

A series of handsheets were formed using PA-2, PA-3, and PA-4 with Pulp II to determine the effect of the molecular weight of the retention aid on the sheet properties. The study also allows comparison with the earlier results on Pulp I and with subsequent experiments using Pulp II on the IPC web former. The data are presented in Table III and the values for the retention are plotted against amount of polymer added in Fig. 9. The vertical bars represent the range of values obtained with the three polymers. No trend with molecular weight was found. This is in agreement with the results obtained earlier using Pulp I. [Compare Fig. 5 of the previous report (1).] It is apparent that a larger amount of the polymer

will be required to reach the maximum attainable retention than was the case for Pulp I, in line with the results of the "pulp titration" experiment above. Data for handsheets when using PEI-2 (Sets 170-173) also indicate a larger requirement for polymer with Pulp II than with Pulp I.

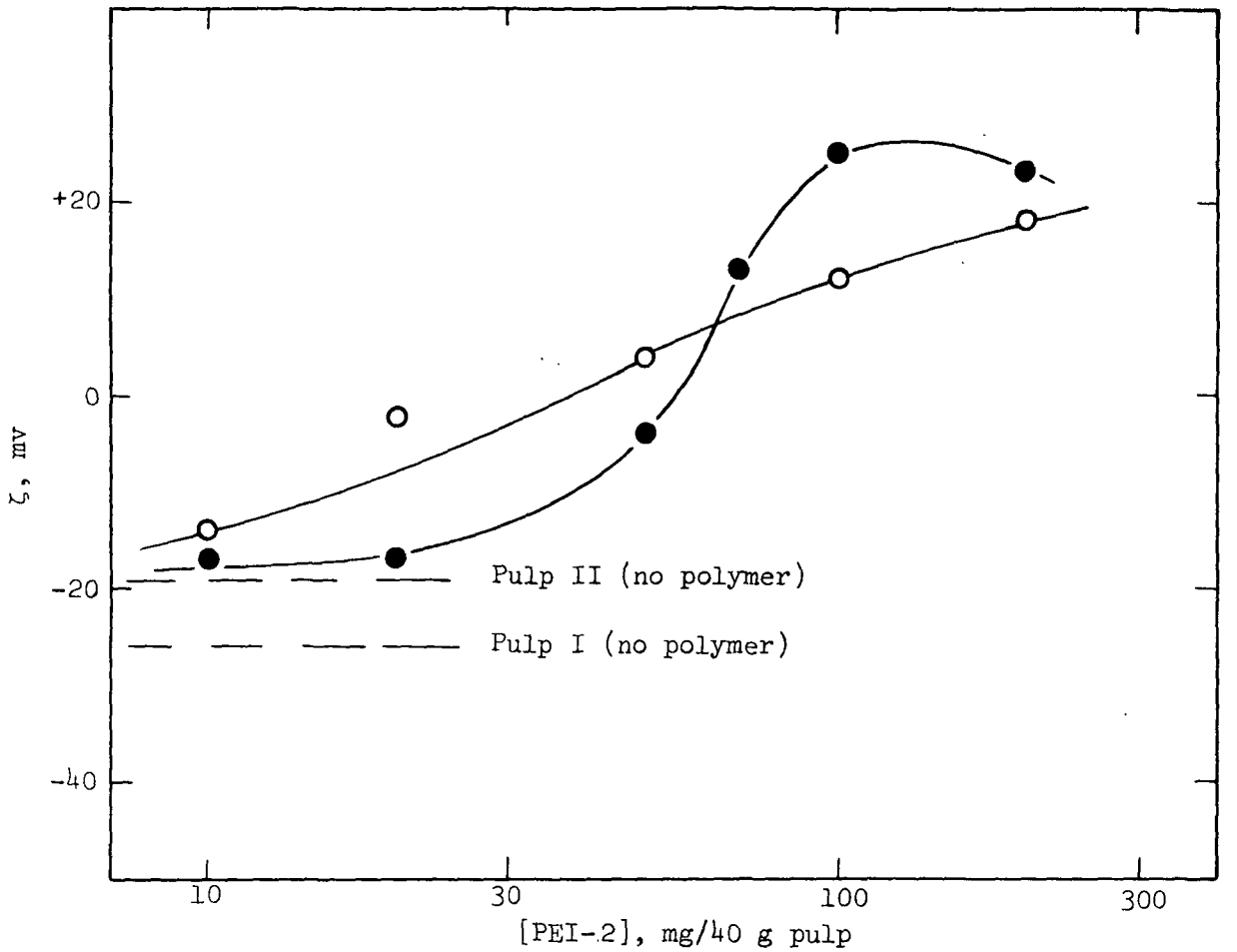


Figure 8. Zeta Potential Plotted Against Logarithm of Polymer Concentration. Open Circles, Pulp I; Filled Circles, Pulp II. Dashed Lines Indicate Levels with No Additives

Another major difference between the two pulps appears when the values for s or s_2 are compared. The scattering efficiency as mirrored by s_2 for the sheets in Table III is more than 1000 cm^2/g lower than the corresponding values for sheets from Pulp I. The decrease can be attributed to the effect of the

increased amount of fines in the case of Pulp II. During sheet formation, or perhaps earlier, they coat the surface of the TiO_2 particles on the fibers thereby reducing the refractive index between the air and the solid leading to a decreased scattering efficiency. The effect of the fines can be seen graphically by comparison of the micrographs in Fig. 5 and 7 (Pulp I) with that in Fig. 10 (Set 162, Pulp II). In the latter figure the TiO_2 particles are not distinct but appear to have a covering of fibrous and amorphous material.

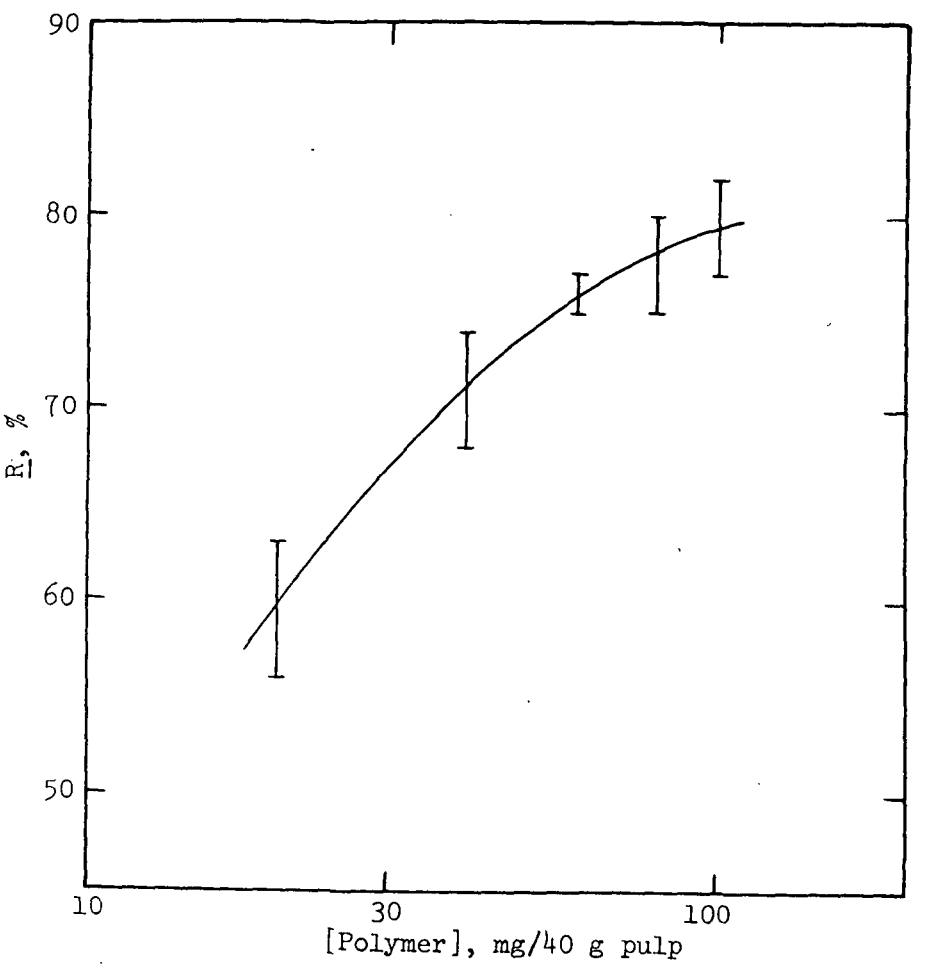


Figure 9. Percent Retention Plotted Against Logarithm of Polymer Concentration. Vertical Bars Represent Range of Values for PA-2, PA-3, and PA-4

Figure 10. SEM Micrograph of Handsheet from Set 162. Magnification 6000X

It is thus seen that the amount of fines in a pulp can have a strong effect on both retention and opacity. The filler adsorbs to a large extent on the fines but by adding sufficient cationic polymer both can be retained. In a highly beaten pulp, however, the scattering efficiency will suffer due to the coating of the well-retained particles by the excess fines.

STUDIES OF RETENTION ON THE WEB FORMER

To determine whether the conclusions reached with the handsheet studies could be extrapolated to higher consistencies and to dynamic conditions more closely simulating those on a commercial paper machine, a series of runs was made with the IPC web former. This machine has been described previously (10) and, although the usual operating conditions are 10-20 feet per min, the drainage forces, rates, and times are comparable (11) to those on a paper machine with a speed of 1000 ft/min.

MATERIALS AND METHODS

The operation of the machine with regard to thin stock preparation was different from that described in the published report (10). In the present experiments the thick stock at 0.7% consistency was diluted at a mixing tee in the pipeline to 0.2% consistency with water from the wire pit. A constant wire speed of 10 ft/min produced a continuous web of paper 12 inches wide with a basis weight of 50 g/m^2 which was pressed and then dried on a single cylinder thereby inhibiting shrinkage in both machine and cross directions. The wire was a 70 × 48 semitwill. For each run four levels of vacuum (26, 40, 50, and 60 cm H_2O) in the suction box were used to vary the drainage rates.

Five pounds of the previously beaten dewatered Pulp II was slushed for 10 min at 2% consistency in a Valley beater with no load. It was then pumped to a stainless steel stock chest and diluted to 0.7%. Enough 7% solids TiO_2(II) suspension was then added to the vortex of the well-stirred pulp slurry to give a filler concentration of 5% based on the o.d. pulp. Tap water with a specific conductance of 210 μmho/cm was used throughout. After pigment addition the pH was adjusted to 5.0 with dilute H_2SO_4, and the stock was stirred for

10 min before initiation of web formation. Dilution water in the wire pit was also adjusted to a pH of 5. Exploratory studies revealed that a 10-min period of machine operation was sufficient to establish a steady state concentration of fines and filler in the wire pit. After allowing time for this initial transient, paper was made at each of the four suction box vacuums. Each run was carried out at a constant level and point of polymer addition.

To determine the effect of molecular weight on the retention process, two cationic polymers, PA-2 and PA-4, with molecular weight of 5×10^5 and $>> 1 \times 10^6$, respectively, were employed. These were introduced at concentrations suggested by the earlier handsheet work at two different points in the stock. In the first method, the polymer was mixed for 5 min with the TiO_2 slurry at a pH of 10 as was done with the handsheet studies, Sets 159-169. The pigment/polymer system was then added to the pulp at 0.7% consistency in the stock chest as described above and the pH was adjusted to 5. A continuous polymer addition was employed in the second method. A 0.1% solution of the polymer under pressure was admitted through a tap into a 1-inch pipe carrying the thick stock to the mixing tee. A capillary rotameter allowed the rate of polymer injection to be monitored. Approximately 8 sec of mixing time elapsed between the point of polymer addition and the mixing tee where dilution with the wire pit water occurred. From here to the slice an additional 10 sec of mixing took place. The furnish did not pass through a pump after the polymer was added. The Reynolds numbers before and after the mixing tee were 6000 and 15,000, respectively, or well into the turbulent regime.

During most runs the forming length or distance from the slice to the dry line was noted at each suction box vacuum level as a measure of the drainage. The reported lengths include an initial distance before the suction box opening

during which no drainage occurs. At the end of a run a sample of the wire pit water was collected for determination of zeta potential. The paper formed under the various conditions was subsequently evaluated for % ash, optical properties, Thwing formation, and tensile strengths in the machine and cross directions.

RESULTS AND DISCUSSION

The data for 13 runs on the web former including operating variables, % ash, white water zeta potential, sheet and pigment specific scattering coefficients, and forming length are listed in Table VII. The corresponding data on the physical properties of the paper produced in these runs are listed in Table VIII in Appendix II. Unless stated to be contrary, the results to be discussed will pertain to runs where the polymer was added to the stock chest (with the TiO_2).

For all the runs the filler retention as judged by the % ash was high. Typical results are shown in Fig. 11 for the effect of polymer dosage on % ash. A maximum in effectiveness is seen at around 0.15% polymer. Increasing the suction box vacuum decreases the amount of filler retained at all polymer concentrations. This is in agreement with the effect of drainage rate on retention found in the pressure sheet mold studies described previously [(1), Fig. 10]. Results similar to those in Fig. 11 were also found when the high molecular weight polymer was the retention aid. No advantage of one polymer over the other in resistance to loss of retention with increase in drainage rate (suction box vacuum) was observed.

Paralleling the decrease in retention with increasing drainage rate is a decrease in the specific scattering coefficient for the sheet s. Representative data are shown in Fig. 12 for a number of different runs. Although the

TABLE VII

WEB FORMER OPERATING AND PAPER PARAMETERS

Run No.	Polymer, %	Suction Box Vacuum, cm H_2O	Ash, %	ζ_w, mv	S, cm^2/g	S_2, cm^2/g	Forming Length, inch
			Pulp Only				
5	None	26	0.17	-19	342		
		40	0.14		338		
		50	0.15		344		
		60	0.18		338		
			PA-2 Added to Stock Chest				
2	0.05	26	4.21	-14	501	4160	
		40	3.90		503	4520	
		50	3.76		484	4170	
		60	3.70		487	4310	
3	0.10	26	3.96	-11	515	4760	
		40	4.05		501	4320	
		50	4.07		502	4320	
		60	3.93		500	4410	
4	0.15	26	4.25	-22	527	4740	
		40	4.05		522	4830	
		50	4.00		519	4820	
		60	3.98		511	4640	
6	0.20	26	4.04	-10	521	4820	4.0
		40	3.92		515	4800	3.4
		50	3.73		510	4900	3.2
		60	3.68		503	4770	3.0
7	0.25	26	4.04	-6	508	4500	3.4
		40	3.90		506	4600	3.1
		50	3.67		508	4920	2.8
		60	3.59		490	4520	2.6
			PA-4 Added to Stock Chest				
8	0.05	26	4.26	-10	475	3510	4.2
		40	4.19		471	3470	3.8
		50	3.95		468	3580	3.5
		60	3.82		468	3690	3.2
9	0.10	26	4.17	-9	497	4110	3.9
		40	4.16		499	4160	3.6
		50	4.00		494	4190	3.4
		60	3.92		489	4140	3.1
10	0.15	26	4.22	-7	524	4700	4.0
		40	4.12		510	4470	3.6
		50	4.06		509	4500	3.4
		60	3.87		511	4760	3.0
11	0.20	26	4.03	-12	506	4460	3.8
		40	3.97		510	4620	3.4
		50	3.73		505	4760	3.2
		60	3.66		491	4470	2.9
12	0.25	26	4.11	-9	514	4570	3.6
		40	4.07		514	4620	3.4
		50	3.92		504	4520	3.1
		60	3.85		504	4600	2.9
			PA-2 Added In-Line				
15	0.15	26	4.52	+11	536	4680	3.9
		40	4.39		533	4740	3.5
		50	4.37		528	4640	3.1
		60	4.39		519	4420	2.9
			PA-4 Added In-Line				
14	0.15	26	4.26	+12	524	4660	3.6
		40	4.25		513	4410	3.4
		50	4.20		508	4340	3.1
		60	4.32		519	4480	2.9

changes are not large, the trends are valid. The results for the other runs exhibit similar behavior.

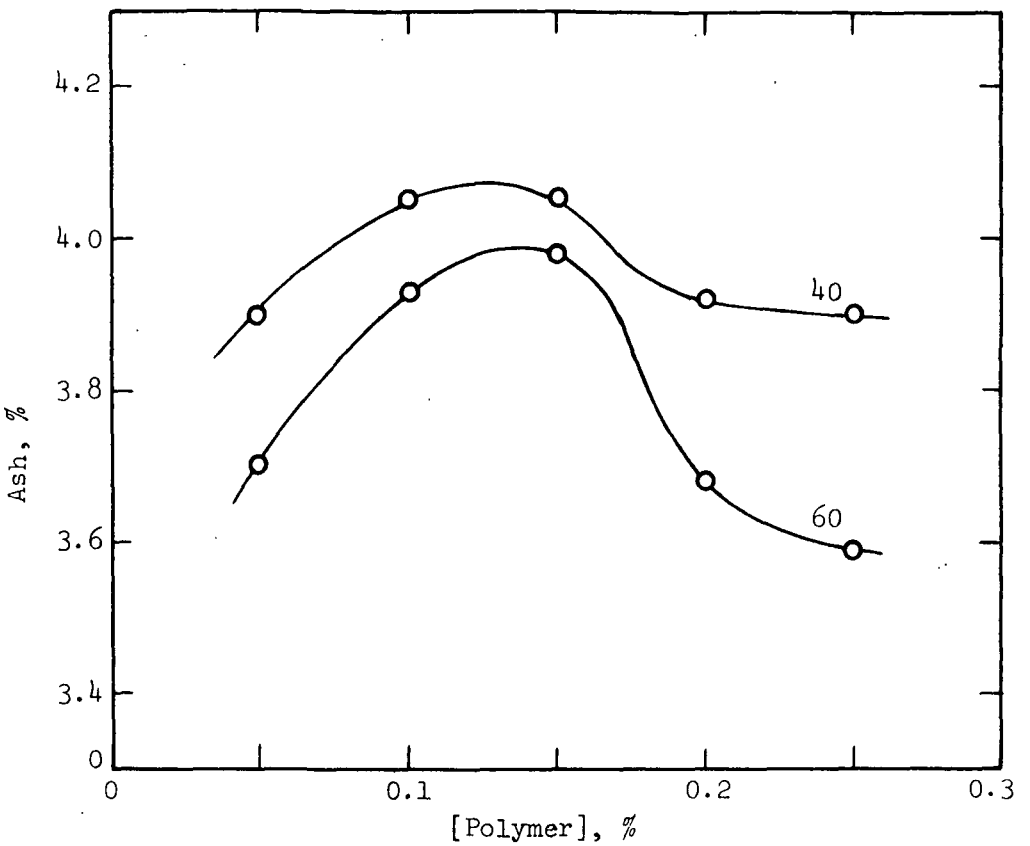


Figure 11. Percentage Ash Plotted Against Concentration of PA-2 Added to the Furnish. The Numbers Identifying Each Curve Indicate the Suction Box Vacuum in cm H_2O

In contrast, the specific scattering coefficient of the pigment $\underline{s}_2$, being related to the ratio of $\underline{s}$ and % ash, does not show any trend with suction box vacuum. However, the data plotted in Fig. 13 do exhibit an optimum value with respect to the amount of polymer present. Propitiously, the maximum in $\underline{s}_2$ occurs at about the same concentration of retention aid as does retention [cf. Fig. 11], so that the maximum opacity can be achieved in this range. From Fig. 13 it is apparent that use of the lower molecular weight polymer leads to slightly higher optical efficiencies. This is likely due to increased TiO_2 flocculation

in the case of the higher molecular weight polymer. In particular for Run 8 (0.05% PA-4) particle aggregation during the initial mixing of TiO_2 and polym as discussed in the handsheet studies above, would appear to be the cause for the low value of $\underline{s}_2$. Scanning electron micrographs bear out this hypothesis. In Fig. 14 the surfaces of paper from Run 8 (26 cm H_2O) and from Run 4 (50 cm H_2O) are compared. Large clumps of TiO_2 are visible in the former, while for the latter, which is near the maximum in Fig. 13, the size of the aggregates smaller, and the distribution of particles is relatively more uniform.

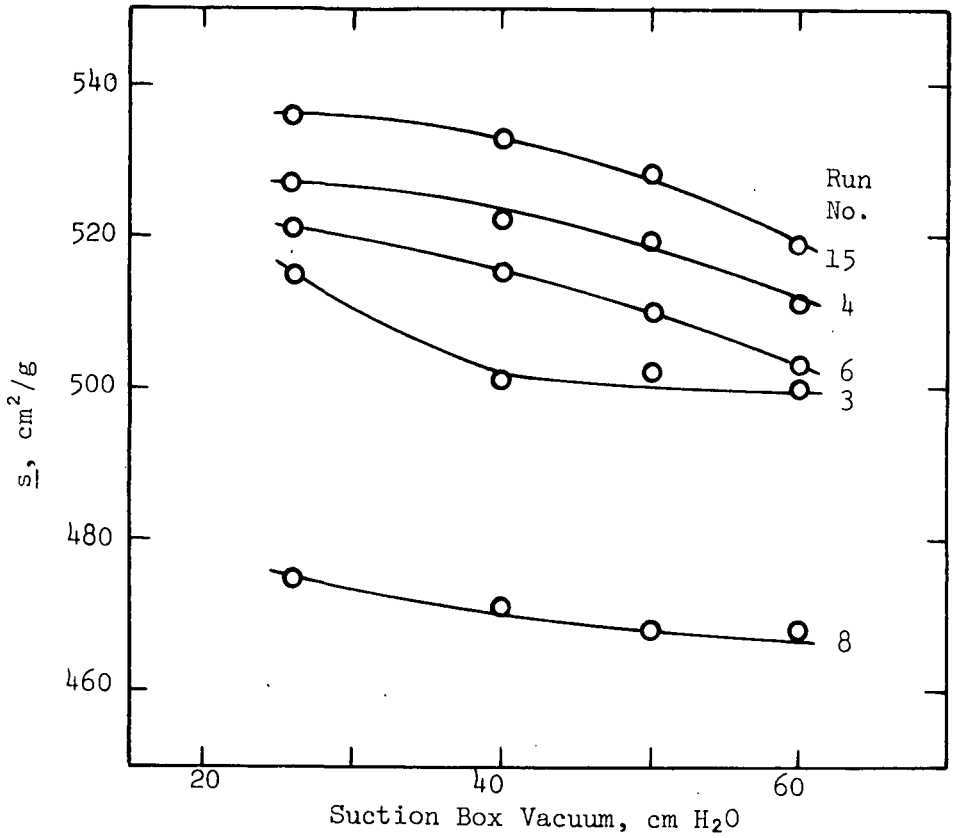


Figure 12. Specific Scattering Coefficient of the Sheet Plotted Against a Measure of the Drainage Rate for the Indicated Runs

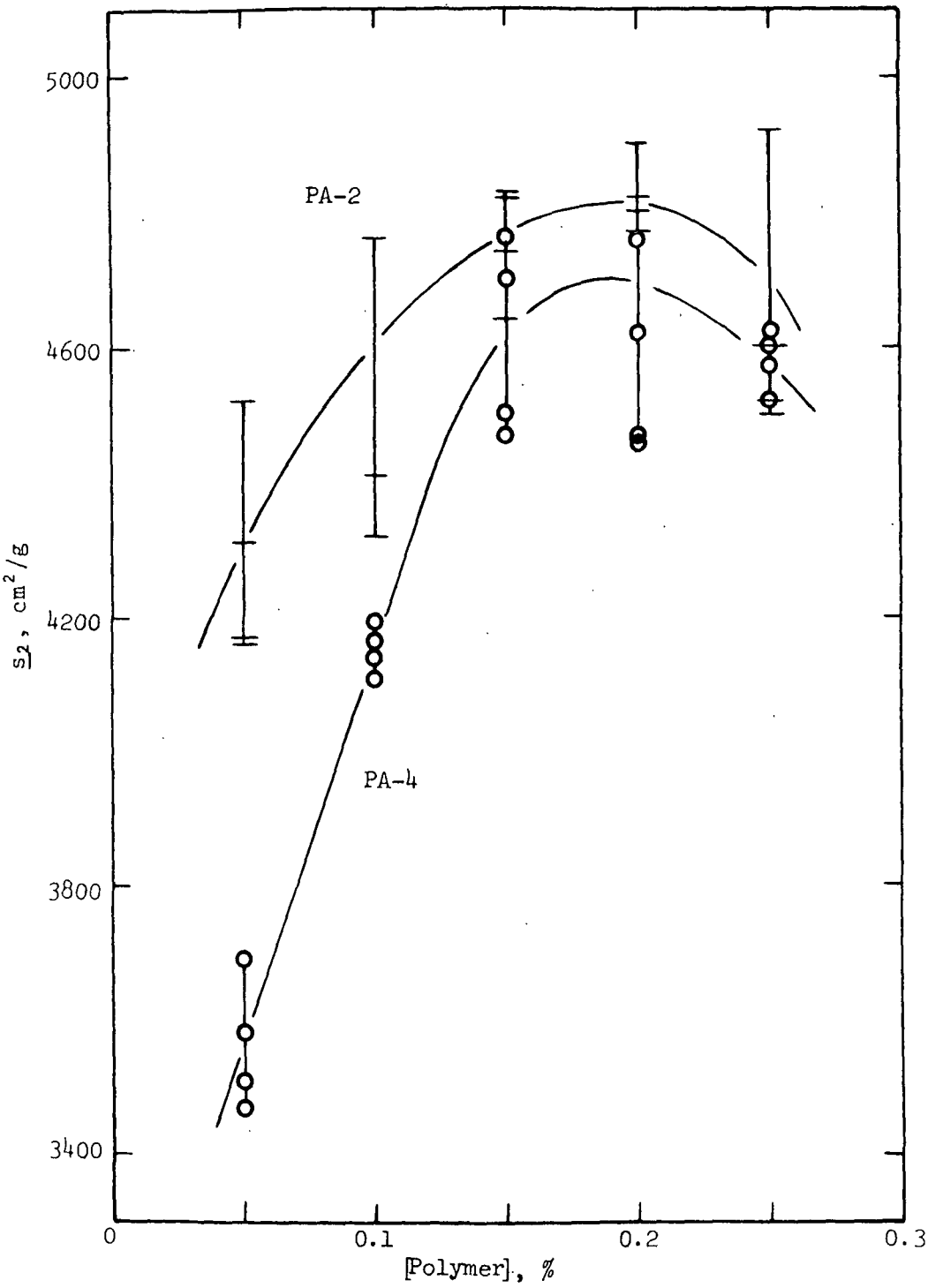
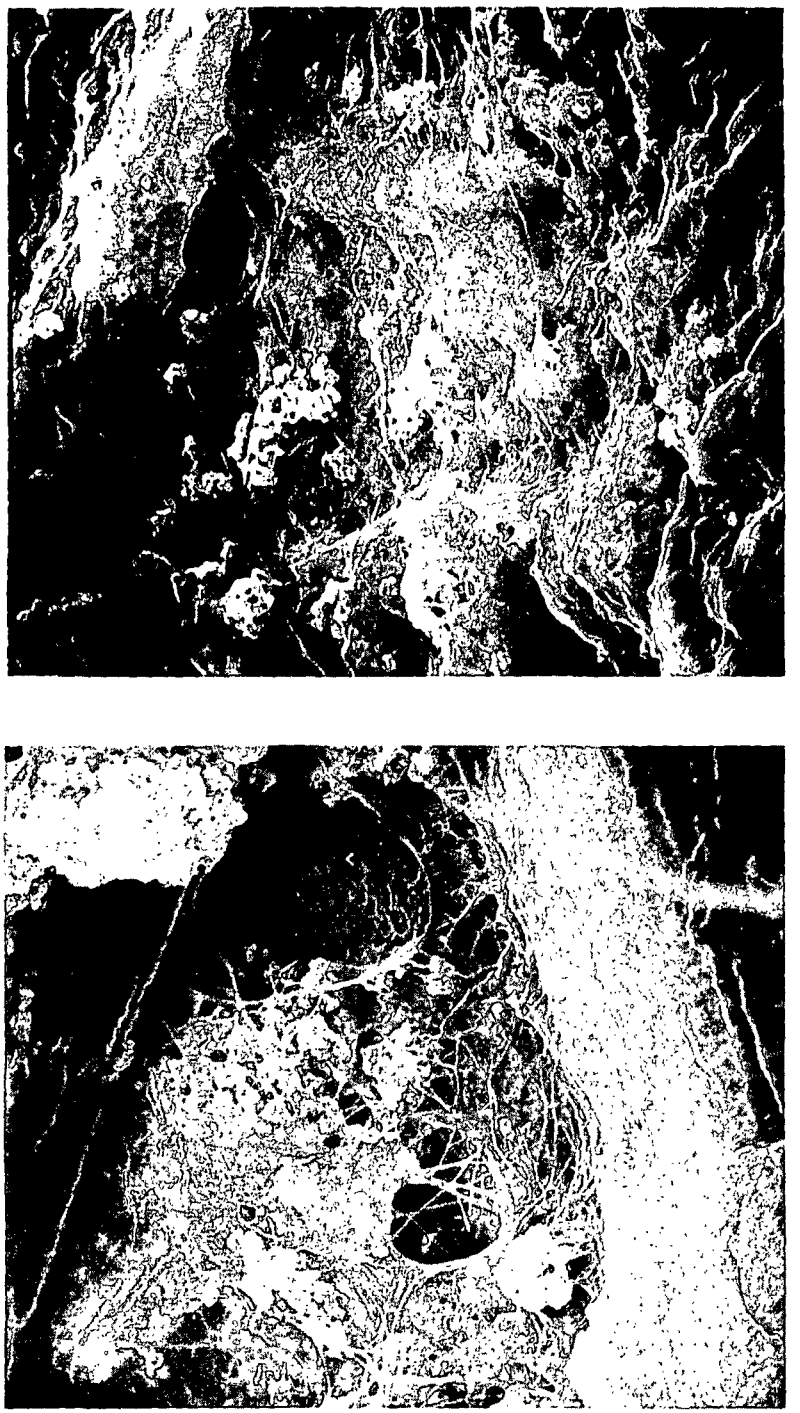


Figure 13. Specific Scattering Coefficient of Pigment Plotted Against Amount of Polymer Added to Furnish. Vertical Bars Represent the Range of Values for Different Suction Box Vacuums. Horizontal Lines (PA-2) and Circles (PA-4) Indicate the Individual Values



b

a

Figure 14. Scanning Electron Micrographs of Paper from Web Former. a) Run 8 (26 cm H_2O), b) Run 4 (50 cm H_2O). Magnification 6000X

It is also notable that the values of $\underline{s}_2$ of paper made on the web former are considerably lower than the corresponding values of handsheets made with the same pulp, TiO_2, and concentration of polymer. For PA-2 the values are: web former, $4160 < \underline{s}_2 < 4920$; handsheet, $5070 < \underline{s}_2 < 5350$. For PA-4 the values are: web former, $3470 < \underline{s}_2 < 4760$; handsheet, $4770 < \underline{s}_2 < 5220$. The differences observed between the two are probably the result of different methods of formation, in particular, a fivefold difference in consistency. Sheet formation at the higher consistency will lead to greater mechanical entrapment of fines with the probability of overcoating the retained pigment particles and thereby reducing their scattering power. Visual evidence for this is contained in Fig. 10 and 14. The concentration of polymer in handsheet Set 162 is the same as that in web former Run 4. The sheets from the web former have a much greater amount of debris on the fiber surfaces. This consists of some fibrils but for the most part is an amorphous membranelike material. In some areas the pigment is completely covered leading to the observed low values of $\underline{s}_2$.

The effect of level of polymer dosage and suction box vacuum on the forming length is presented in Fig. 15 for PA-4. Predictably, the dry line moves back toward the slice with increasing suction box vacuum. A steady increase in drainage with increasing amount of polymer means that it is not possible to optimize filler retention and drainage simultaneously. The reason that the forming length is still decreasing at the highest polymer addition level may be related to the finite, albeit small, negative white water zeta potentials for these samples. A rule-of-thumb is that the optimum drainage will occur at a zeta potential of zero. Further work will be required to determine whether this is a valid explanation for the present results.

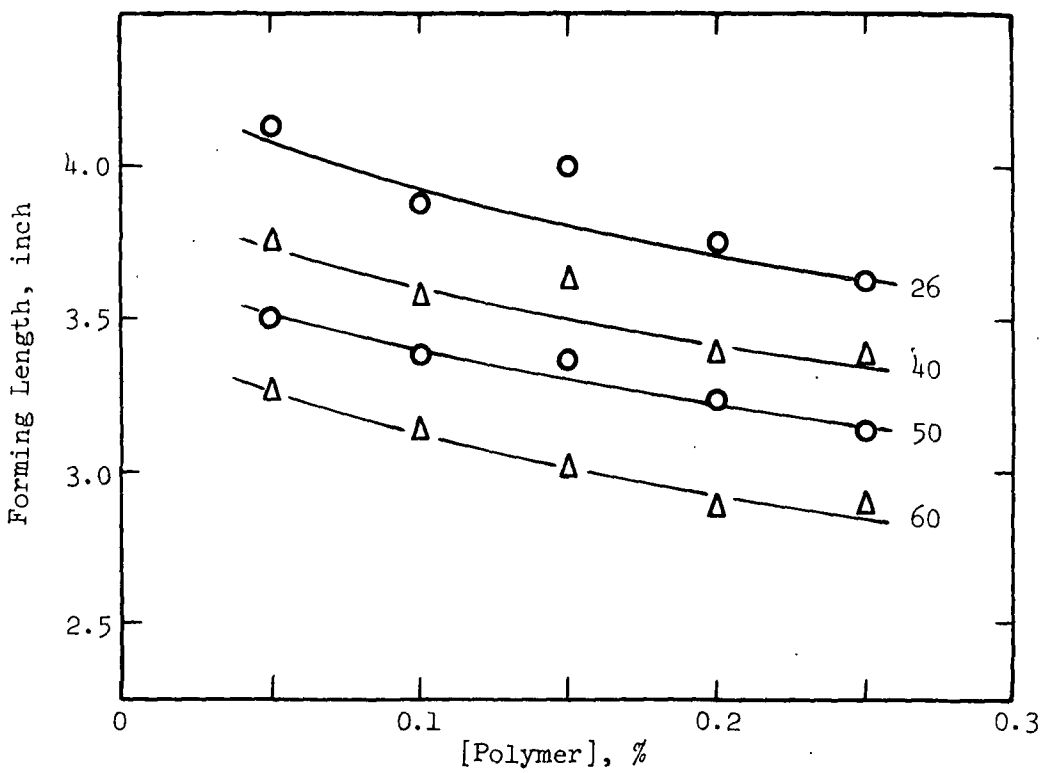


Figure 15. Forming Length Plotted Against Amount of PA-4 Added to Furnish at the Indicated Suction Box Vacuums in cm H_2O

The effect of addition of the polymer in-line will be considered next. The differences between the two methods of addition are, for the most part, very small. In-line addition appears to produce slightly higher % ash, $\underline{s}$, and drainage but slightly lower $\underline{s}_2$. In addition, the % ash does not seem to be so strongly dependent on the level of the suction box vacuum as do the corresponding results when the polymer is added to the stock chest. Most of these results are barely outside experimental error and further replications would have to be performed to determine whether the differences are statistically significant. On firmer ground are the conclusions concerning zeta potential and Thwing formation. In-line addition gives a moderately positive zeta potential, in agreement with the earlier handsheet studies where addition of the polymer to the deckle box likewise gave a positive zeta potential. Apparently, the factors leading to a negative zeta

potential in Runs 2-12 require longer than the 18-sec residence time from point of polymer addition to the slice for action. The other parameter unambiguously displaying a dependence on the mode of polymer addition was the Thwing formation. Upon comparison of Runs 4 and 15 and of Runs 10 and 14, it is obvious that addition of the polymer in-line produces some flocculation of the pulp leading to poorer formation. It is likely that any such floc formation occurring in the stock chest addition method is irreversibly destroyed by the prolonged agitation (> 20 min) at a high agitation rate (Lightnin' mixer). On a commercial paper machine with proper headbox design floc formation should not be a problem.

The tensile breaking strength for the paper made on the web former has a MD/CD ratio of about 2:1. No trends with polymer addition level, retention aid molecular weight, suction box vacuum, or formation could be discerned.

CONCLUSIONS

1. The zeta potential can be used to correlate the effective charge density of a polyelectrolyte with the amount of that material necessary to provide maximum retention with a given pulp.

2. Pigment is initially retained on the pulp fines (mostly) and provision must be made for retention of the fines in order to achieve effective pigment utilization.

3. The amount of retention aid required to produce a maximum in filler retention may not provide the best drainage conditions.

SUMMARY OF CONCLUSIONS

In addition to the findings above based on the data in this report, it will be useful to reiterate some of the salient conclusions reached in previous reports.

1. Flocculation of TiO_2 suspensions does not require complete charge neutralization. Formation of small, strongly positive patches of cationic polyelectrolyte which can interact with the generally negative surfaces of other particles is sufficient. Indeed, sufficient polymer to provide charge neutralization usually is beyond that required for restabilization.

2. Molecular weight of the retention or flocculation aid is an insignificant factor with respect to its effectiveness at least for those polymers with a relatively high charge density.

3. The white water zeta potential is a product of complex interactions between filler, fines, polymer, polyvalent anions, and filler dispersant. Nevertheless, useful correlations may be obtained with it if it is employed only as a rough measure of the electrokinetic conditions in the furnish.

4. For those polymers whose degree of charge is dependent on pH, the optical efficiency of a filler can be a strong function of the pH at the point of polymer addition. This is because under some conditions, the polymeric retention aid leads to particle aggregation (flocculation) before being retained by the fibers and fines.

5. For polymers with high charge density, resistance to loss of pigment retention by hydrodynamic shearing during sheet formation was not a function of polymer molecular weight.

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APPENDIX I

POLYMER IDENTIFICATION

Code	Polymer (Manufacturer)
PEI-1	Polyethylenimine, research sample, SA 1117 (Dow Chemical Co.)
PEI-2	Tydex 12 (Dow Chemical Co.)
PA-1	Magnifloc 560C (American Cyanamid Co.)
PA-2	Cationic polyacrylamide, research sample, $M = 5 \times 10^5$ (Dow Chemical Co.)
PA-3	Cationic polyacrylamide, research sample, $M = 1 \times 10^6$ (Dow Chemical Co.)
PA-4	Cationic polyacrylamide, research sample, $M >> 10^6$ (Dow Chemical Co.)
R-3	Reten 300 (Hercules Inc.)
B-6	Bubond 64 (Buckman Laboratories, Inc.)
Modified guar	Gendriv 162 (General Mills Chemicals, Inc.)
Chitosan	(Food, Chemical, and Research Laboratories, Inc.)

APPENDIX II

WEB FORMER PAPER DATA

TABLE VIII

PAPER PHYSICAL PROPERTIES

Run No.	Suction Box Vacuum, cm H_2O	Thwing Formation	Tensile Breaking Length, m MD	Tensile Breaking Length, m CD
		Pulp Only		
5	26	37.8	8800	4130
	40	39.2	8690	4070
	50	39.9	9160	4250
	60	40.1	8690	4260
		PA-2 Added to Stock Chest		
2	26	44.8	8150	4170
	40	44.6	8100	3840
	50	43.1	8150	3850
	60	44.1	7900	3950
3	26	44.2	8250	3900
	40	45.2	8280	4000
	50	44.5	8130	3830
	60	44.0	8450	3940
4	26	42.0	8150	3960
	40	41.5	8010	3990
	50	39.7	7830	3790
	60	39.7	8130	3980
6	26	46.3	8280	3860
	40	46.2	8100	3880
	50	44.5	7980	3830
	60	44.2	7860	3920
7	26	44.5	8250	3960
	40	43.9	8200	4020
	50	41.2	7830	4020
	60	39.3	7830	3890
		PA-4 Added to Stock Chest		
8	26	43.6	8250	3830
	40	43.2	8350	3860
	50	42.2	8200	3940
	60	42.5	8160	3850
9	26	46.9	8150	3830
	40	45.9	8280	3920
	50	46.0	8130	4030
	60	46.4	8010	4040
10	26	45.5	7690	3860
	40	44.2	7600	3690
	50	45.0	7410	3710
	60	45.5	7560	3800
11	26	45.9	7860	3750
	40	45.9	8050	3880
	50	45.0	7800	4010
	60	44.5	7540	3820
12	26	44.2	8310	4070
	40	45.5	7710	3850
	50	43.9	7650	3900
	60	45.1	7310	3900
		PA-2 Added In-Line		
15	26	33.4	8150	3730
	40	34.9	7900	3720
	50	34.2	7830	3750
	60	33.7	7600	3640
		PA-4 Added In-Line		
14	26	40.6	7860	3560
	40	40.8	7710	3580
	50	40.1	7800	3600
	60	38.4	7600	3400